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MACRO/MICRO GRADIENT OF SOLUTE CONCENTRATION DURING SOLIDIFICATION OF THE Ni/Al/Ni INTERCONNECTIONS

MAKRO/MIKRO GRADIENT STĘŻENIA PODCZAS KRYSZALIZACJI ZŁĄCZA Ni/Al/Ni

A new model of the formation of the diffusion interconnections has been proposed. Formation of the diffusion interconnection consists of dissolution, solidification and homogenization. Dissolution is treated as a process leading to creation of 1D solid — liquid system closed for the mass exchange. Also the nominal concentration of the Al-solute for solidification is obtained as a result of the dissolution. Subsequently, a solidification is shown as a process beginning at the nominal solute concentration. The nominal concentration is placed on the *liquidus* line of the Ni-Al phase diagram and applied to the solidification model. Solidification produces different intermetallic phases in sequence so that macro-gradient related to average solute content of the area centre within the all phases is considered. A development of micro gradient of the Al-solute content within each intermetallic phase is also studied. Both macro and micro gradients are shown due to simulation of the solidification for the Ni-Al-Ni interconnection of the nominal solute content measured in the experiment.

Zaproponowano model kształtowania się złącza dyfuzyjnego. Formowanie złącza następuje w etapach i składa się z rozpuszczania składników, krystalizacji oraz homogenizacji. Rozpuszczanie jest traktowane jako zjawisko kształtowania się jednowymiarowego układu faza ciekła — faza stała, zamkniętego dla wymiany masy. Również, stężenie nominalne składnika stopowego jest wynikiem rozpuszczania. W rezultacie takich założeń, krystalizacja jest pokazana jako proces startujący od stężenia nominalnego, które jest ułożone na linii *likwidus* diagramu Ni-Al i użyte w modelu krystalizacji. W wyniku krystalizacji powstają różne fazy i związki międzymetaliczne w sekwencji wynikającej z diagramu fazowego. Istnieje zatem makro-gradient stężenia odniesiony do środków barycentrycznych

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wszystkich faz jakie powstają w procesie krystalizacji. Dodatkowo, powstawanie mikrogradientu stężenia w obrębie danej fazy również może być analizowane z zastosowaniem modelu. Obydwa gradienty makro- i mikro- są pokazane stosownie do symulacji procesu krystalizacji w odniesieniu do złącza Ni/Al/Ni o stężeniu nominalnym zmierzonym w eksperymencie.

1. Introduction

A formation of the diffusion solder occurs in such a way that average content of the solute, N_0 , does not change within the produced sub-layers of intermetallic phases, independently of a stage of the isothermal solidification at which the process is stopped. The average content of the Al-solute resulting from the dissolution of nickel in the liquid aluminium during the process of diffusion soldering can be applied to the simulation as a nominal Al-solute content. Both amount of intermetallic phases within the interconnection and solute segregation across them should be similar in simulation and experiment, [1]. Therefore, diffusion soldering of the Ni/Al/Ni system occurring at the constant temperature equal to 680°C and under vacuum was stopped for different periods of time and Al-solute segregation measured.

The $25\text{ }\mu\text{m}$ thick Al-foil was used in the experiment. The samples were frozen in cold argon stream. The morphology and Al — solute segregation profile were revealed by the SEM/EDS analysis for different time of solidification process and N_0 — parameter was measured. The average value of the N_0 — parameter is equal to about 0.66 [mole fr.] when technological temperature applied in experiment, T_R , is constant and equal to 680°C , Fig. 1.

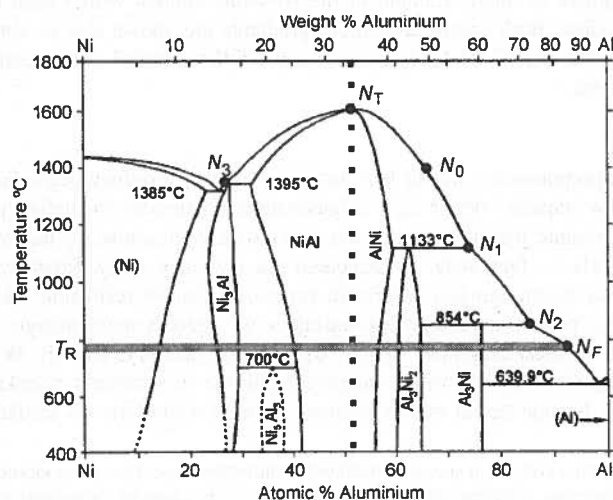


Fig. 1. Position of the technological temperature, T_R , superposed on the Ni-Al phase diagram, [6] and resulting nominal concentration of the solute, N_0

The measured N_0 — parameter will be used in the simulation of solidification process in order to reproduce amount of growing sub-layers, segregation profile across them and finally for estimating macro/micro gradient of solute concentration.

2. Theoretical reproduction of the solute segregation profile

The experimentally estimated N_0 parameter can be introduced to the following relationship:

$$\Delta\lambda_{32}/\Delta\lambda_{31} = (k_3N_2 - N_0)/(N_0 - k_2N_1), \quad (1)$$

where

$\Delta\lambda_{32}$ is the thickness of the Al_3Ni_2 peritectic phase sub-layer, and

$\Delta\lambda_{31}$ is the thickness of the Al_3Ni peritectic phase sub-layer.

The present model is able to reproduce the experimental ratio, equation (1) by means of the theoretical ratio:

$$\frac{\Delta\lambda_{32}}{\Delta\lambda_{31}} \approx \frac{x_1^{\max} - x_1^{\min}}{x_2^{\max} - x_2^{\min}}. \quad (2)$$

The x_i^{\max} and; x_i^{\min} ; ($i = 1,2$) parameters introduced to the equation (2) have the following definitions:

$$x_i^{\max}(\alpha_i^D, \alpha_i^P, k_i, k_{i+1}) - x_i(\alpha_i^D, k_i) = A_i(\alpha_i^P, k_i) [x_i(\alpha_i^P, k_{i+1}) - x_i(\alpha_i^P, k_i)], 0 \leq A_i \leq 1 \quad (2)$$

where

$A(0, k_i) = 0$ for non-equilibrium formation sequence of peritectic phases,

$A(1, k_i) = 1$ for equilibrium formation sequence of peritectic phases (lever rule).

$$\int_0^{x_i^{\min}} [N_i^B(x + x_i - x_i^{\min}, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i) - N_i^B(x, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i)] dx + \int_{x_i^{\min}}^{x_i} [k_{i+1}N_i - N_i^B(x, x_i, \alpha_i^D, l_i^0, N_{i-1}, k_i)] dx = (N_i - k_{i+1}N_i) [x_i^{\max}(\alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i, k_{i+1}) - x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i)]. \quad (3)$$

The theoretical reproduction of the measured profile of the Al – solute segregation is based on the scheme shown in Fig. 2. According to the scheme the liquid interlayer resolidifies as a result of interaction between liquid filler metal and solid substrates. Under above circumstances, the joining technology can result in a interconnection that reproduces several intermetallic compounds and phases in sequence resulting from a given equilibrium phase diagram, [2, 3].

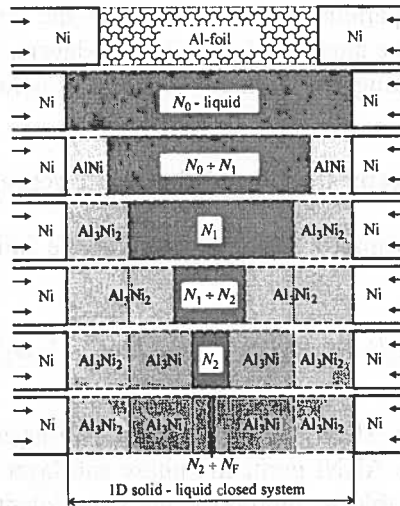


Fig. 2. Simplified scheme of the ranges of virtual solidification for the formation of the Ni-Al-Ni interconnection

The microstructural development is assumed to involve three processes: solute dissolution, solidification and homogenisation, [4]. The solute dissolution precedes the solidification, [5] and therefore, in the current model is treated as a process for creating the nominal solute concentration, N_0 , (Fig. 2), for solidification.

In the experiment two peritectic phases Al_3Ni_2 and Al_3Ni are forming. Thus, simulation should at least have possibility to reproduce both mentioned peritectic phases.

According to the model which is referred to the solidification path $N_0 \div N_F$, Fig. 1, simulation reproduces the phases in three ranges: $N_0 \div N_1$; $N_1 \div N_2$ and $N_2 \div N_F$.

The liquid obtained due to dissolution then subjected to virtual solidification within the $N_0 \div N_1$ range, Fig. 2, leads to precipitation of the AlNi primary phase.

At the N_1 — solute concentration in the liquid the first peritectic reaction completely or almost completely consumes the precipitated AlNi — phase. As a result, Al_3Ni_2 — phase sub-layer appears as a first real component of the joint, Fig. 3. Since the second primary phase appears due to the virtual solidification within the range, $N_1 \div N_2$, the amount of the Al_3Ni_2 phase increases, Fig. 2. At the N_2 — solute concentration in the liquid the second peritectic reaction completely or almost completely consumes the precipitated Al_3Ni_2 — phase. As a result, Al_3Ni phase sub-layer appears as the second real component of the joint. If additionally, the Al_3Ni phase appears due to solidification within the range, $N_2 \div N_F$ its total amount increases, Fig. 2. Finally, small amount of the N_F — liquid remains just at the centre of joint. It satisfies the mass balance of the solute within the solid — liquid system as closed virtually for mass exchange, Fig. 2.

The simplified scheme, Fig. 2, explains the sequence reactions as if it occurred within the whole gap between two Ni — substrates. In real joint, the above reactions

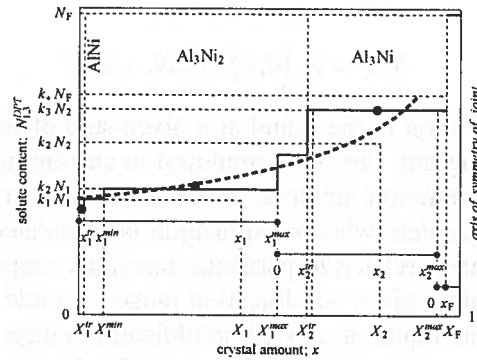


Fig. 3. Al — solute segregation profile within Al_3Ni_2 and Al_3Ni sub-layers just at the end of solidification accompanied by both solid/solid transformations; dashed line defines the average solute content of the area centre of sub-layers

occur within the infinitesimally small amount of the liquid to form dx amount of the solid. The process of dissolution / solidification is repeated many times and finally consumes all the liquid.

The Al_3Ni_2 phase of the N_0^{32} average solute concentration is produced from the liquid of the N_0 concentration of Al — solute. Its diffusion controlled growth occurs just at the boundary Ni — substrate / Al_3Ni_2 phase sub-layer itself. The Al_3Ni phase of the N_0^{31} average solute concentration is produced from the liquid of the N_1 nominal concentration of the Al — solute. Its growth occurs just at the boundary Al_3Ni phase sub-layer itself / liquid. So, the discussed general N_0 concentration of the liquid, Fig.2 is the weight average of both N_0^{32} and N_0^{31} local nominal solute concentrations in the both solid, respectively.

It is evident that according to the theorem of maximum driving force the Al_3Ni_2 phase grows first as well as the N_0^{32} local nominal concentration forms first, [7].

The ratio: amount of the Al_3Ni_2 phase / amount of the Al_3Ni phase should be constant during solidification and results in general N_0 concentration of solute.

Consequently, the boundary between sub-layer of Al_3Ni_2 phase / sub-layer of Al_3Ni phase is stable during the period of time required by solidification process.

An equation fundamental for the description of solute redistribution, N_i^B , after solidification process accompanied by the back-diffusion is given as follows:

$$\begin{aligned} N_i^B(x, x_i^0, \alpha_i^D, l_i^0, N_{i-1}, k_i) &= [1 + \beta_i^{\text{ex}}(x, x_i^0, l_i^0, k_i) \beta_i^{\text{in}}(x_i^0, \alpha_i^D, l_i^0, k_i)] \times \\ N_i^S(x, \alpha_i^D, l_i^0, N_{i-1}, k_i), \end{aligned} \quad (4)$$

where

$$N_i^S(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) = k_i N_i(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) \quad (5)$$

and

$$N_i(x, \alpha_i^D, l_i^0, N_{i-1}, k_i) = N_{i-1} [(l_i^0 + \alpha_i^D k_i x - x) / l_i^0]^{1 - \alpha_i^D k_i} \quad (6)$$

with

$$N_{i-1} = N_i \left(0, \alpha_i^D, l_i^0, N_{i-1}, k_i \right) \quad (7)$$

N_i is the solute concentration in the liquid at a given step of solidification, [1].

The Ni-Al phase diagram, Fig. 1, is employed in current model formulation with:

N_0 Al — solute concentration, nominal for the solidification process,

N_F final Al — solute content when solidification is completed, Fig. 1,

N_1, N_2 Al — solute content related to peritectic reactions, respectively, Fig. 1,

k_i partition ratio within a given solidification range, i , [mole fr. / mole fr.],

l_i^0 initial amount of the liquid at a given solidification range, i , dimensionless,

i a given solidification range between the points N_0-N_F , ($i = 1, 2, 3$), Fig. 1,

N_{i-1} solute content at the beginning of a given solidification range, i , [mole fr.],

x current amount of a growing sub-layer, dimensionless,

x_i^0 amount of growing sub-layer for an imposed freezing process, dimensionless,

α_i^D back-diffusion parameter for partitioning and redistribution, dimensionless,

β_i^{ex} coefficient for the extent of redistribution, dimensionless, [1],

β_i^{in} coefficient for the intensity of redistribution, dimensionless, [1].

The above phenomena taken into account in simulation as virtual processes are accompanied by peritectic reactions. In the case of analysed interconnection two peritectic reactions should be analysed:

a/ first reaction: $AlNi + liquid(N_1) \Rightarrow Al_3Ni_2$,

at the N_1 — solute concentration, and

b/ second reaction: $Al_3Ni_2 + liquid(N_2) \Rightarrow Al_3Ni$

at the N_2 — solute concentration, as marked in the Ni-Al phase diagram, Fig. 2.

Four different examples of simulation have been made using the above mode of calculation, Figs 3-6. The Al - solute segregation profile is simulated under condition: a/ AlNi phase is not completely consumed during first peritectic reaction and two s/s transformations ($AlNi \rightarrow Al_3Ni_2$ and $Al_3Ni_2 \rightarrow Al_3Ni$) occurred simultaneously with solidification from adequate ranges of solute concentration in the liquid ($N_1 \rightarrow N_2$ and $N_2 \rightarrow N_F$) respectively; an amount of the remaining liquid is observed at the interconnection centreline, Fig. 3, according to the mass balance in the considered closed system shown in Fig.2,

b/ AlNi phase is completely consumed during first peritectic reaction and the second s/s transformation ($Al_3Ni_2 \rightarrow Al_3Ni$) occurred simultaneously with solidification from adequate range of solute concentration in the liquid ($N_2 \rightarrow N_F$); an amount of the remaining liquid is observed at the interconnection centreline, Fig. 4, according to the mass balance in the considered closed system shown in Fig.2,

c/ AlNi phase is completely consumed during first peritectic reaction and no s/s transformations; the Al_3Ni_2 phase is not completely consumed during the second peritectic reaction; an amount of the remaining liquid is observed at the interconnection centreline, Fig. 5, according to the mass balance, Fig.2,

d/ AlNi phase is completely consumed during first peritectic reaction and no s/s transformations; the Al_3Ni_2 phase is completely consumed during the second peritectic

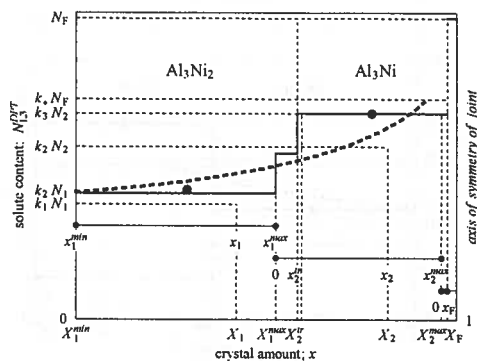


Fig. 4. Al — solute segregation profile within Al_3Ni_2 and Al_3Ni sub-layers just at the end of solidification accompanied by the second solid/solid transformations only; dashed line defines average solute content of the area centre of sub-layers

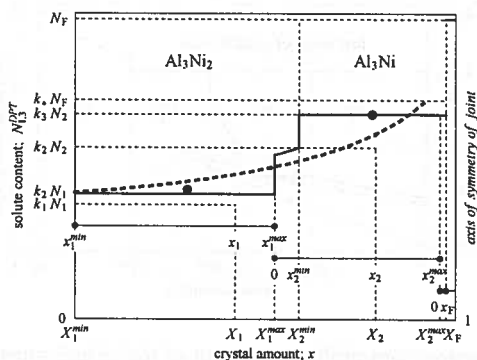


Fig. 5. Al — solute segregation profile within Al_3Ni_2 and Al_3Ni sub-layers just at the end of solidification; no solid/solid transformations; the Al_3Ni_2 phase not completely consumed during the second peritectic reaction; dashed line defines the average solute content of the area centre of sub-layers

reaction; no remaining liquid is observed at the interconnection centreline, Fig. 6; solidification is completed at the N_2 solute concentration in the liquid, Fig. 1.

It is to be emphasized that final profile of solute segregation, Figs 3-6, are the result of superposition of: a/ curve representing the partitioning (thin line in Fig. 7), b/ curve representing the primary redistribution due to the back-diffusion associated with the partitioning (dashed line in Fig. 7),

c/ curve representing the secondary redistribution due to diffusive shift required by occurrence of peritectic reaction (bold N_1^D and dotted N_1^T lines in Fig. 7), d/ curve representing the solid/solid transformation (bold N_1^T lines in Fig. 7), e/ curve representing the peritectic reaction (bold N_1^P line in Fig. 7).

The micro-gradient of solute concentration can be analysed for each from among all curves plotted in Fig. 7, as they are simulated to build up the final profile, Figs 3-6

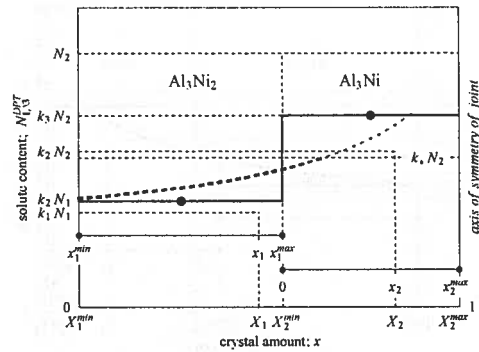


Fig. 6. Al — solute segregation profile within Al_3Ni_2 and Al_3Ni sub-layers just at the end of solidification completed at the N_2 solute concentration in the liquid; no solid/solid transformations; no remnant liquid; dashed line defines the average solute content of the area centre of sub-layers

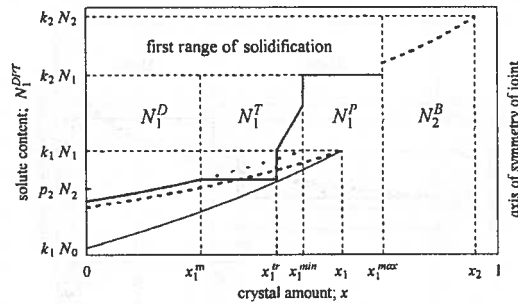


Fig. 7. The N_1^{DPT} — solute segregation profile as a result of the virtual superposition of the partitioning (thin line) primary (dashed line) and secondary (thick N_1^D — dotted N_1^T line) redistributions, peritectic reaction (thick N_1^P line) and solid/solid transformation (thick N_1^T line) as considered in the current model of the joint formation

3. Concluding remarks

The micro-gradient of the solute concentration can be analysed in relation to the microsegregation resulting from partitioning, primary solute redistribution and secondary solute redistribution resulting from back-diffusion plotted for one stage of solidification, Fig. 7.

The virtual superposition of microsegregation and primary as well as secondary solute redistributions forms the real segregation profile related to peritectic reaction, finally.

The micro-gradient of solute redistribution diminishes significantly to be equal to zero at the peritectic reaction, Fig. 7. It suggests that back-diffusion is very rapid into each infinitesimally small amount of growing solid, dx , and ensures the equilibrium solidification within.

Therefore, it is evident that formation sequence of both considered peritectic phases Al_3Ni_2 and Al_3Ni could be simulated using equation (4) but referred to phase diagram with two metastable *solidus* lines with partition ratio: $k_i^m = k_{i+1}$, $i = 1, 2$ and with the application of the back-diffusion parameter, $\alpha_i^D = 1$, as required by equilibrium solidification.

Both analyses of behavior of micro-gradient of solute concentration and virtual superposition of microsegregation and primary as well as secondary solute redistributions proves that real formation of the interconnection occurs through the metastable solidification process.

The four results of simulation are shown in order to choose the simulated, final solute segregation profile similar to experimental profile of segregation.

The profile of the solute segregation shown in Fig. 5 seems to be the most adequate to the experimental profile observed within the joint obtained with the use of the Al-foil (15 μm thick) at $T_R = 720^\circ C$, [8].

Dashed lines (Figs 3-6) representing average solute content of the area centre within the sub-layers give information about macro-gradient of solute redistribution for a given thickness of foil used in the experiment.

The average solute content curves are drawn using an optimizing procedure as if primary redistribution occurred at average partition ratio equal to k_* and α_* — average back-diffusion parameter.

The average solute content curves are fitting the area centre of the all sub-layers with good accuracy.

It is suggested to not to calculate the segregation profile resulting from the s/s transformations because s/s transformation is time consuming process and cannot occur during solidification which requires about 2 minutes time, only.

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